

1966 (continued)

59. Chem. Abstr. 65, 16112e, 1966.

Use of the secondary ion-ion emission method in the study of ammonia decomposition on iron. V. I. Silvaliko and Ya. M. Fogel (State Univ., Kharkov). *Kinetika i Kataliz* 7(4), 722-6 (1966)(Russ). Decompn. of NH_3 on pure Fe (99.99% Fe) was studied at room temp. to 800° and NH_3 pressure of 1×10^{-4} mm. using the previously described secondary ion-ion emission method (CA 60, 12698k). Only oxide-free Fe surface catalyzes the decompn. of NH_3 . Fe surface covered with Fe oxides is inactive in the decompn. of NH_3 . The proposed mechanism of the decompn. of NH_3 on Fe is identical with the previously proposed for the decompn. of NH_3 on Pt (*loc. cit.*). GPJR

60. Chem. Abstr. 64, 13439h, 1966.

The change of the rate-determining step of the ammonia decomposition over an ammonia synthetic iron catalyst. N. Takezawa and I. Toyoshima (Hokkaido Univ., Sapporo, Japan). *J. Phys. Chem.* 70(2), 591-5 (1966)(Eng). Evidence is presented that suggests that, even on a particular catalyst, the mechanism is dependent on exptl. conditions. The decompn. was studied in a flow system over a catalyst of 4.72% Al_2O_3 , 0.31% K_2O , and 0.05 SiO_2 , using He as diluent. At 424° the rate could be expressed approx. as $V = k_1(P_{\text{NH}_3}/P_{\text{H}_2})^{0.4}$, which is compatible with Temkin and Pyzhov's mechanism, which assumes the rate detg. step is desorption of adsorbed N (CA 35, 7273g). At 479° the expression for the rate was $V = k_2(P_{\text{NH}_3}/P_{\text{H}_2})^{0.75}$, which suggests that the rate detg. step is the dehydrogenation of adsorbed amino radicals as proposed in the theory of Floriuti (Enomoto and H., CA 47, 7741h).

61. Chem. Abstr. 65, 9794e, 1966.

Rate-determining step of ammonia decomposition over a well-reduced doubly promoted iron catalyst. Nobutsune Takezawa and Isamu Toyoshima (Hokkaido Univ., Sapporo, Japan). *J. Res. Inst. Catalysis Hokkaido Univ.* 14(1), 41-58 (1966)(Eng). The rate of NH_3 decompn. over a well-reduced doubly promoted Fe catalyst was followed in a flow system by using a bench scale reactor. The rate V depends on partial pressures P_A and P_H of NH_3 and H_2 as, $V = k_1(P_A/P_H)^{0.5}$ about 420° , $V = k_2(P_A/P_H)^{0.5}$ above 479° , where consts. k_1 , k_2 , α , and β depended sensitively on the exptl. conditions. At or above 517° , the rate was depressed by N slightly but perceptibly, whereas not at all at a lower temp. The rate-detg. step of NH_3 decompn. changes with rise of reaction temp. from the desorption of N adatoms to 1 of the steps of dehydrogenation of NH_3 on catalyst surface. RCTT

62. Chem. Abstr. 65, 11391g, 1966.

Effect of alkaline promoter on the decomposition of ammonia over the doubly promoted iron catalyst. N. Takezawa and I. Toyoshima (Hokkaido Univ., Sapporo, Japan). *J. Catalysis* 6(1), 45-7 (1966)(Eng); cf. CA 64, 13440u. The catalyst used contained a lower proportion of K_2O than in the previous expts. The kinetic study was made at 378° in a flow system using a differential reactor and 1 atm. total pressure. The rate V of NH_3 decompn. is expressed as $V = K(P_{\text{NH}_3}/P_{\text{H}_2})^{0.4}$. The rate-detg. step of the decompn. changes with the K_2O content of the promoter. The slow step is presumed to be the dehydrogenation of the adsorbed- NH_2 group. S. G. Zipp

1966 (continued)

60. Chem. Abstr. 65, 1435h, 1966.

General rule of the catalytic activity of metals. Kenichi Tanaka and Kenji Tamaru (National Univ., Yokohama, Japan). *Kinetika i Kataliz* 7(2), 242-7 (1966)(Russ). The heat of formation of higher oxides related to 1 α -atom of metal ($-\Delta H_f$) was found to characterize not only the heat of chemisorption of gases on metals but as well the behavior of metals in various catalytic reactions (e.g., NH_3 and HCO_2H decompn. and C_2H_4 hydrogenation on metals). ΔH_f may be correlated with catalyst activity, the reaction order, the kind of mutual interaction of the adsorbate and metal, and with activation energy. 15 references. L. Schanel

1967

61. Chem. Abstr. 67, 76601a, 1967.

76601a Chemical reactions and salts as refrigerants. I. V. Kudryashov, N. I. Gusev, and S. D. Kamyshechenko (Mosk. Khim.-Tekhnol. Inst. im. Mendeleeva, Moscow). *Zh. Fiz. Khim.* 41(5), 967-70 (1967)(Russ). A series of NH_3 salts can be employed as cooling media utilizing the endothermic effect of their decompn. The following salts were studied by thermography by using the photorecording Kurnakov pyrometer FPK-59: NH_4NO_3 , NH_4Br , $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , NH_4HCO_3 , NH_4F , and $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and also their mixts. of varying compn. A series of the salts was studied in the presence of MnO_2 catalyst. The kinetics of MeOH decompn. was studied at 200, 300, and 400° on various catalysts and the kinetics of NH_3 decompn. on a promoted Fe catalyst at 400, 450, 500, 550, and 600° .

Reaction	Temp. range	Endothermic effect, kcal./kg.
$\text{NH}_4\text{Br} \rightarrow \text{NH}_3 + \text{HBr}$	213-245	461
$\text{NH}_4\text{HCO}_3 \rightarrow \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}$	200-214	518
$2\text{NH}_4\text{NO}_3 \rightarrow 2\text{NH}_3 + 2\text{NO}_2 + \text{H}_2\text{O} + 1/2\text{O}_2$	222-242	754
$\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl}$	323-341	785
$\text{NH}_4\text{F} \rightarrow \text{NH}_3 + \text{HF}$	263-282	983
$(\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow 2\text{NH}_3 + \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$	300-340.7	1106
$\text{MeOH} \rightarrow \text{CO} + 2\text{H}_2$	150-100	1000
$\text{MeOH} \rightarrow \text{HCOH} + \text{H}_2$	320	1000
$\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + 3\text{H}_2$	300	500
$\text{NH}_3 \rightarrow 1/2\text{N}_2 + 3/2\text{H}_2$	400-600	800
$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	350-550	1600
$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$	—	—
$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	500-800	1000
$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	250-350	1100
Glycerol vaporization	290	135
Na vaporization	883	1005

M. Shalef

62. Chem. Abstr. 68, 117472a, 1968.

117472a The determination of the rate-determining step of ammonia decomposition by the use of nitrogen-15 as tracer. Akiro Kazusaka and Kazunori Tanaka (Hokkaido Univ., Sapporo, Japan). *Radioisotopes* (Tokyo) 16(3), 103-9 (1967)(Japan). Kinetic studies were made on the decompn. of NH_3 at 470° on a doubly promoted Fe catalyst. Of the three elementary reactions, (1) $\text{NH}_3 \rightarrow \text{N} + 3\text{H}$, (2) $2\text{H} \rightarrow \text{H}_2$, and (3) $2\text{N} \rightarrow \text{N}_2$, reaction (3) was the rate-detg. step and the observed values were close to unity. The relative rate of (1) to (2) varied from 4 to 11 depending on the pressure of NH_3 . Reaction (1) is suggested to be the rate-detg. step at higher temps. since the values obtained at 470° are much smaller than those at 430° (CA 63, 12371e).

C. Urakami

1967 (continued)

1968

3. Chem. Abstr. 69, 22425u, 196865. Chem. Abstr. 69, 30511j, 1968.

22425u Mechanism of catalyzed decomposition of ammonia in the presence of commercial doubly promoted iron catalyst. Takezawa, Nobutsune; Toyoshima, Isamu (Hokkaido Univ., Sapporo, Japan). *J. Res. Inst. Catal., Hokkaido Univ.* 1967, 15(2), 111-26 (Eng). Kinetic observations on NH_3 decompn. by the present authors are analyzed in terms of a generalized theory of reaction rate under the assumption that the decompn. proceeds through the sequence of steps, $\text{NH}_3 \rightarrow \text{NH}_2(a) + \text{H}(a)$, $\text{NH}_2(a) \rightarrow \text{NH}(a) + \text{H}(a)$, $\text{NH}(a) \rightarrow \text{N}(a) + \text{H}(a)$, $2\text{N}(a) \rightarrow \text{N}_2$, and $2\text{H}(a) \rightarrow \text{H}_2$, where (a) signifies the adsorbed state. The rate of decompn. is formulated by allowing for repulsive interactions among adsorbates inclusive of the crit. complexes of the rate-detg. step by the proportional approxn. From the observed pressure dependences of the rate on NH_3 , H_2 , and N_2 , it is concluded that the rate-detg. step of the decompn. around 425° is the desorption of N adatoms $2\text{N}(a) \rightarrow \text{N}_2$, which is consistent with the observation of stoichiometric no. of the rate-detg. step. This conclusion is further confirmed by the agreement of the activation heat of decompn. deduced according to the conclusion with observation and by the agreement of the no. of sites of the crit. complex similarly derived with the crystallographic value. The pressure dependences of the rate around 480° , on the other hand, lead to the conclusion that the rate-detg. step is the dehydrogenation of the adsorbed amino group, $\text{NH}_2(a) \rightarrow \text{NH}(a) + \text{H}(a)$. The rate-detg. step thus shifts with rise of temp. from the desorption of N adatoms to the dehydrogenation of adsorbed amino group. RCTT

30511j Proved methods for studying nickel catalysts. II. Merkel, Heinrich (Heinrich Koppers G.m.b.H., Essen, Ger.). *Brennst.-Chem.* 1968, 49(4), 115-20 (Ger). The chemisorption of CO on optimally reduced comm. Ni catalysts was detd. If the amt. of chemisorbed CO is calcd. for each g. of Ni, the adsorption isotherms for the various Ni catalysts can be arranged in the same sequence as for the NH_3 -decompn. activity (also related to 1 g. Ni). This indicates that for the NH_3 -decompn. and very likely for hydrocarbon synthesis also, the same Ni centers are active as for the chemisorption of CO. Phys. resistance within the porous structure will affect this result. By using the sp. chemisorption, the part of the Ni that occurs in active form on the surface of the catalyst can be calcd. in a simple manner. Depending on the pore structure and other variables, the active part may be 100% or less than 50%. In the case of the chemisorption of CO, some of the Ni centers that occupy the less accessible pores are still active, whereas, in general, these centers are no longer active for the NH_3 decompn. On the other hand, for very low concn., all the Ni that is distributed throughout a suitable porous structure is active for both processes. Subsequent deposition of Ni on the porous structure, however, is only partially effective as some of the already active sites will be covered. In the case of H_2 , only a very small amt. is chemisorbed on Ni catalysts. A comparison of the adsorption isotherms for CO with the formulas of Langmuir, Freundlich, or Temkin shows that for each isotherm there exists a pressure range in which one of the three formulas is obeyed. D. G. Oei

4. Chem. Abstr. 67, 36742v, 1967.66. Chem. Abstr. 69, 90222a, 1968.

36742v Effect of iron catalyst on the kinetics of ammonia decomposition in silent electric discharge. M. V. Tovbin, T. P. Kozlova, and N. A. Perekhod. *Khim. Prom. Ukr.* (Russ. Ed.) 1967(1), 11-12(Russ.), cf. *Ch.* 60, 11415f. The kinetics of decompn. of NH_3 by the simultaneous action of silent discharge and the Fe_2O_3 67.48, Fe 25.04, Al_2O_3 4.75, CaO 0.23, K_2O 2.3, and SiO_2 0.15% catalyst was studied at various temps. The decompn. rate, K , increased linearly with the current and was temp. independent at $28-300^\circ$. At low ($250-325^\circ$) temps. K was detd. by the amt. of NH_3 decompd. in the discharge whereas at $>500^\circ$ it was detd. by the kinetics of the catalytic process. In the intermediate temp. region ($360-425^\circ$), K exceeded that which should be expected from additivity of the catalyst and discharge action. Presumably, at those temps. the decompn. of NH_3 molcs., excited by a discharge, occurred to active centers of the catalyst surface. Thus, in synthesis and in decompn. of NH_3 the mechanism of action of the catalyst in the silent discharge is the same. J. L. Kornacki

90222a Ammonia-decomposition catalyst. Sobolevskii, V. S.; Golosman, E. Z.; Chistozvonov, D. B.; Lytkin, V. P.; Galkina, A. I. U.S.S.R. 210,837 (Cl. B 01j), 08 Feb 1968, Appl. 11 Feb 1966; From *Izobret., Prom. Obratzy, Tovarnye Znaki* 1968, 45(7), 17. A catalyst based on Fe for the dissociation of NH_3 , guaranteeing the prepn. of a gaseous mixt. with an NH_3 content of 0.02-0.03% is produced by alloying magnetite with Al_2O_3 and by promoting with CaO, SiO, and K_2O . The compn. (in %) of the catalyst is as follows: Fe oxide 48-9, Al_2O_3 47-9, CaO 1.35-1.4, SiO₂ 0.35-0.4, and K_2O 0.5-0.6. MQCL

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